

Characterization of Coal Fly Ash Associated with a Release of Fly Ash at TVA's Kingston Fossil Plant

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TVA, TDEC, and EPA performed soil and ash sampling in the former Dredge Cell, in the embayment, and at several private residences following the release. The objectives of the soil and ash sampling were to characterize the chemical nature of the ash, determine if the released ash resulted in residual impacts to native soil, and evaluate the potential threat of the released ash to human health and the environment. In addition, characterization of recovered ash was done to assess disposal options and to guide potential remediation activities. In early 2010, borings made in a nearby geologic layer ("Knox Group") were sampled to compare to overlying soil.

TVA Sampling

TVA collected eight ash samples from private residential properties adjacent to the KIF site on December 27, 2008 through January 2, 2009. On December 31, 2008, TVA collected five surface ash samples from ash remaining in the former Dredge Cell and 23 subsurface ash samples from one Geoprobe® vertical profile within the intact Dredge Cell. These ash samples (locations S-1 through S-5 and the Geoprobe® location) were analyzed for benzene, toluene, ethylbenzene, and total xylenes (BTEX) by EPA SW-846 Method 8260; total metals by EPA SW-846 Method 6010B; mercury by EPA SW-846 Method 7471; and TCLP metals by EPA SW-846 Methods 1311 and 6010B. A total of 19 five-point composite ash samples were collected on January 6 and 12, 2009, from the released ash in Swan Pond Embayment. These samples (locations AFA-1 through AFA-19) were analyzed for total metals by EPA SW-846 Method 6010B.

Residual sample media were returned to TVA and sent to separate laboratories for reanalysis of metals utilizing a more vigorous microwave digestion (EPA Method – 3051). Eleven supplemental ash samples (EECA-1 through EECA-11) were collected in September 2009 from the Dredge Cell and embayment area and analyzed for polynuclear aromatic hydrocarbons (PAHs), mercury, and radioisotopes.

In February 2009, submerged samples of ash and ash mixed with sediment adjacent to the spill site at Emory River Mile (ERM) 2.1, sediment samples from ERM 0.5 as well as upstream sediment samples at ERM 6, 7, and 9 were collected and analyzed for a similar suite of metals as those in the intact cell, EECA and AFA sets.

PAHs

PAHs are not anticipated to be present in the ash due to the conditions under which the coal is combusted (e.g., high temperature, oxygen rich environment). TVA conducted confirmatory analytical sampling for PAHs in September 2009; and as anticipated, PAHs were not detected, except for 2-methylnaphthalene in a single ash sample. That sample was collected from an area of the ash that has had substantial regrading and movement of ash by heavy equipment. Therefore, the presence of 2-methylnaphthalene is likely attributable to deposition from equipment exhaust. The 2-methylnaphthalene detection was slightly greater than the reporting limit. Re-extraction and reanalysis did not confirm the presence of 2-methylnaphthalene above the reporting limit.

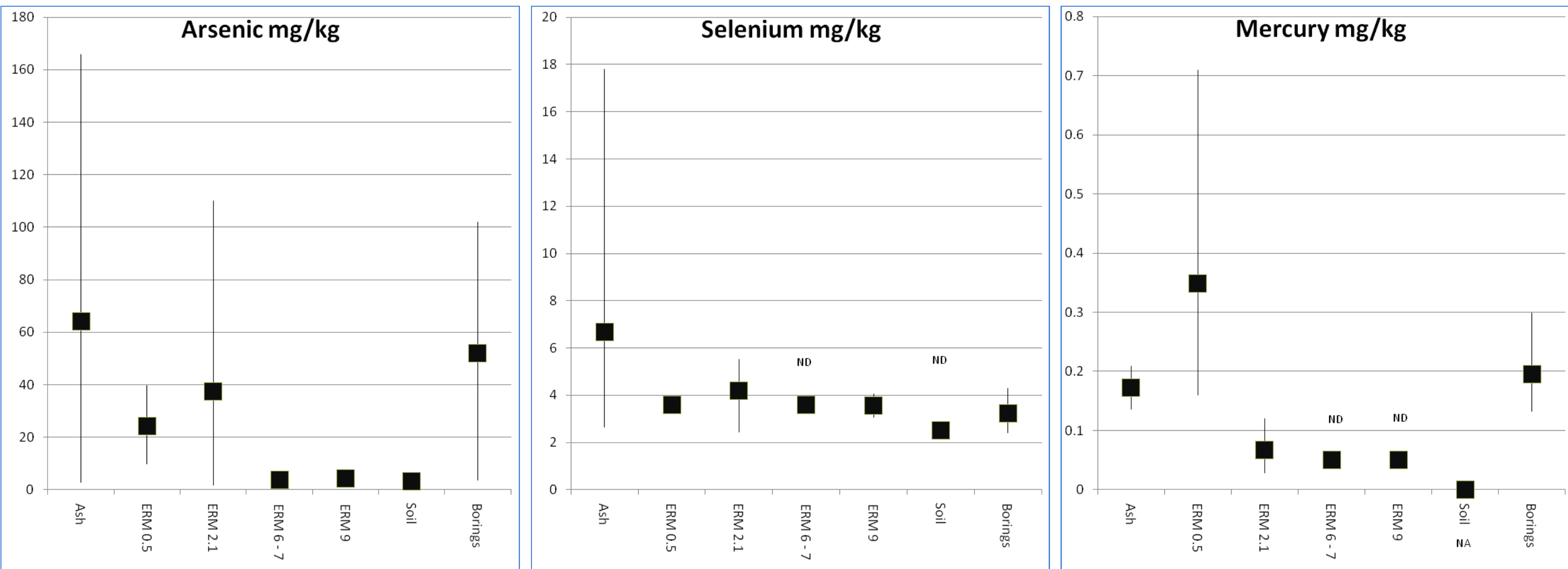
Metals and Metalloids

The following analytes are considered constituents of interest (COI) related to fly ash: arsenic, chromium, copper, lead, mercury, nickel, selenium, thallium, vanadium, zinc, and the naturally occurring radionuclides, specifically isotopes of ura-

nium and thorium, their short-lived daughter products, and potassium-40.

In the following set of graphs, results for these elements are compared as min, max, average plots of the various elements expressed in mg/kg. Groupings plotted are "Ash" which consists of the AFA, EECA, Geoprobe®, and S-x series, ERM 2.1, ERM 0.5, Residence soil, ERM 6 through 7, ERM 9 and the borings into the Knox Group. Non-detects are plotted at the detection limit and indicated by "ND".

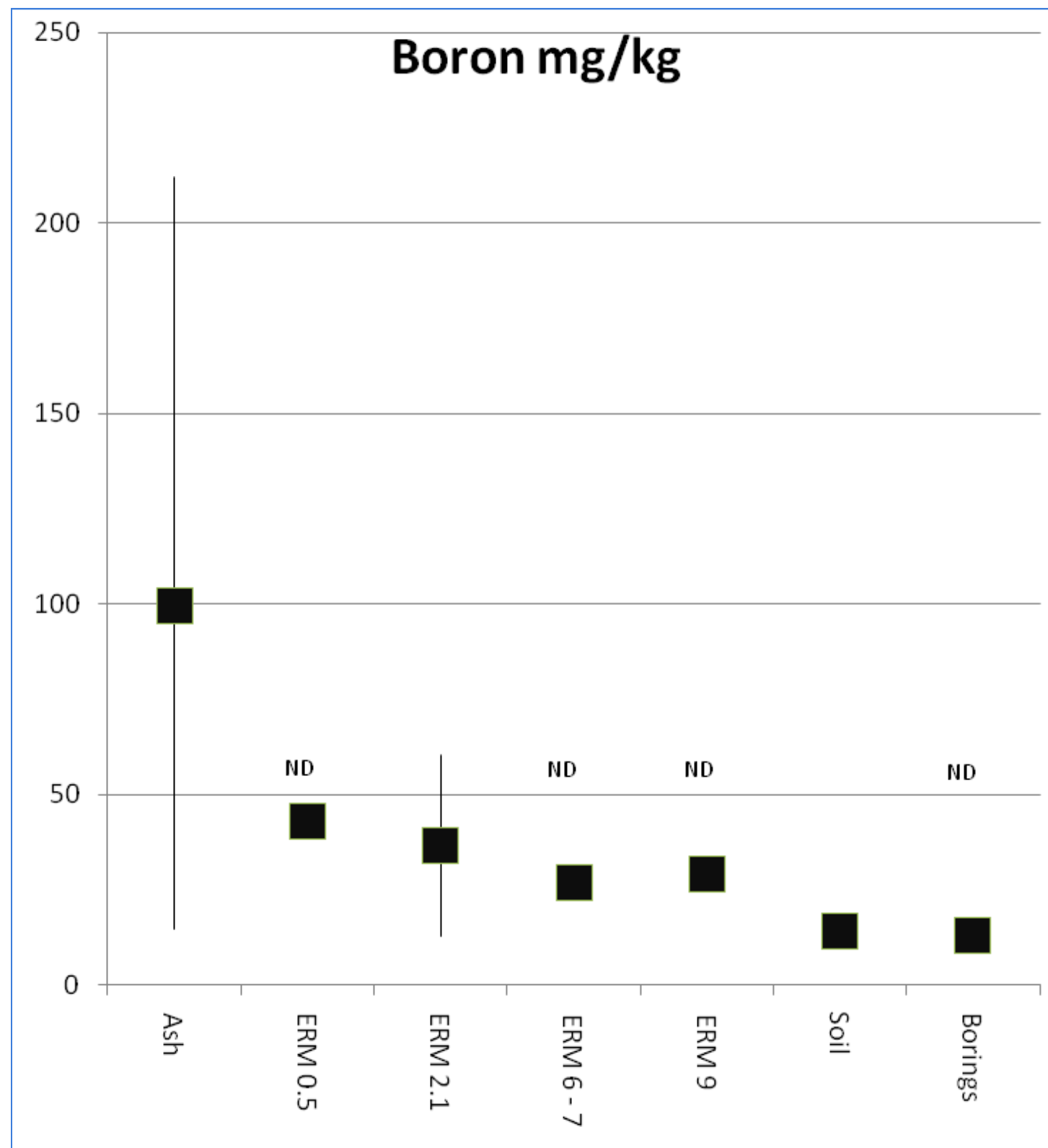
Arsenic is significantly higher in the ash samples (intact cell, EECA, AFA, etc.) and submerged samples at ERM 2.1 than the local residence soil and in the upstream sediment samples. Downstream sediment appeared to be slightly lower in concentration than the ash samples. Surprisingly, the results from the Knox Group stratum were significantly higher than overlying soil. Arsenic is one of the naturally-occurring trace elements concentrated in ash through the coal combustion process. Arsenic is a known human carcinogen routinely detected in ash samples at concentrations that may be a concern for human exposures. As such, arsenic may be considered to represent the constituents within the ash. Arsenic concentrations in ash samples collected by TVA ranged from 2.78 to 166 milligrams per kilogram (mg/kg), with an average of 65 mg/kg. However, arsenic is widely distributed in the natural environment. Arsenic levels for soils typical of the Roane County region range from 6.4 to 655 mg/kg. Arsenic concentrations reported in TVA ash samples are within the range of concentrations reported for soil. However, three samples in the Department of Energy (DOE) dataset are elevated relative to all other results. These concentrations (180, 512, and 655 mg/kg) are considered valid results based on a review of the information on the sample locations presented in DOE's report. While the concentrations do not appear to have been influenced by DOE operations (including waste disposal), they may have been influenced by past agricultural activities. Therefore, while these values are suspect due to potential anthropogenic impacts they are indicative of the range of arsenic concentrations in native and agricultural soil in the region. Levels in the ash are therefore similar to those of typical regional soils. It should be noted that ash is not natural soil, and therefore direct comparisons to "background" concentrations cannot be made. These comparisons are only meant to provide a framework for recognizing differences or similarities between the ash constituents and those found in typical regional soils.



Other naturally-occurring trace elements in ash also show results greater than would be expected in typical regional soils but few values exceeded maxima documented in a statewide soil survey (TDEC 2001). Barium, beryllium, boron, selenium, and vanadium were detected in more than 80% of the ash samples and at maximum concentrations that are greater than maximum levels for soils typical of the Roane County region. Similarly, essential dietary nutrients such as potassium and sodium were also detected at maximum concentrations greater than those for typical regional soils. Selenium was more widely variable in the ash samples and the average was elevated compared to sediment, soil and geologic samples.

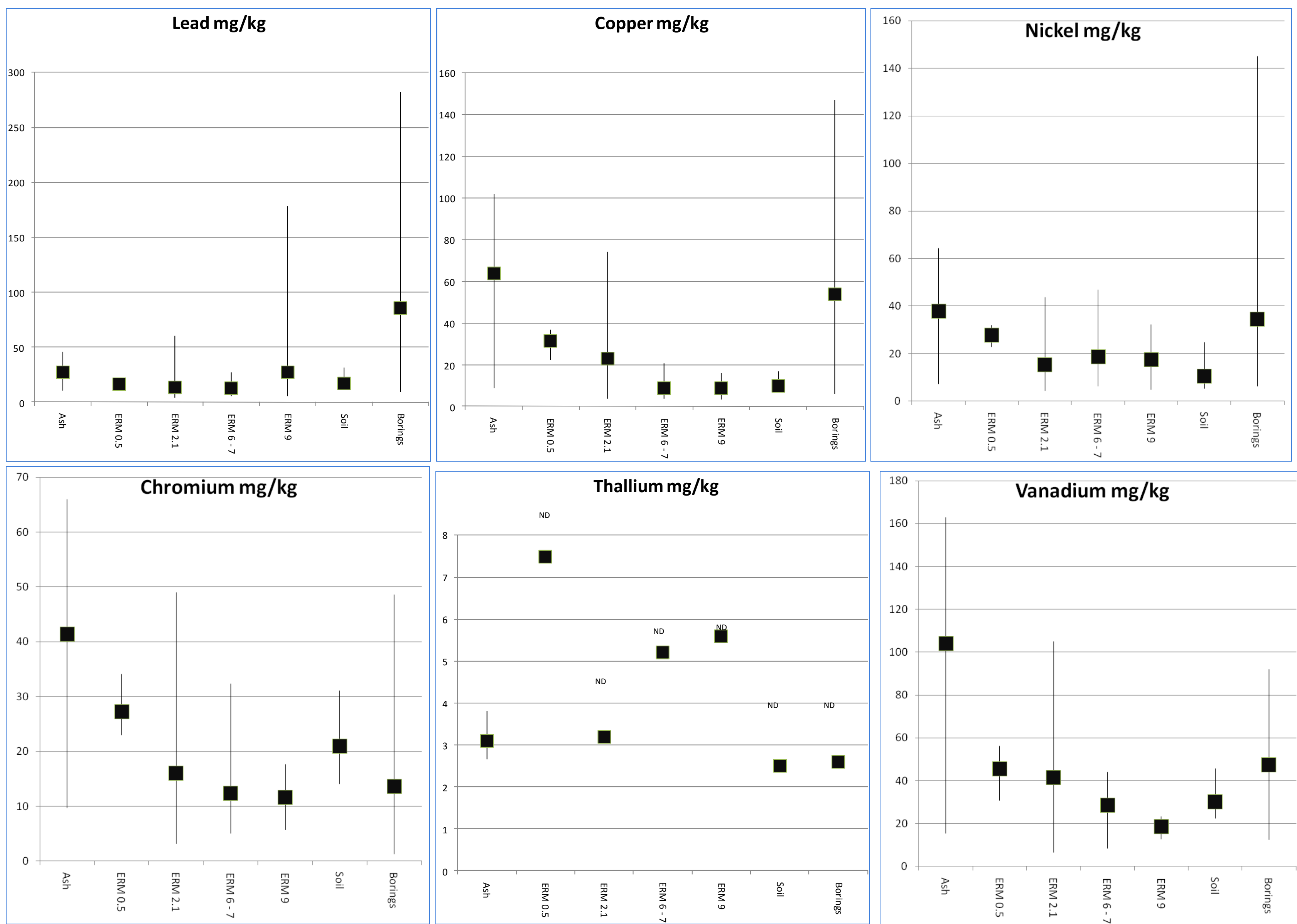
Mercury values were low (4 detects out of 61 ash samples) except those at ERM 0.5 where backflow from the Clinch has allowed mercury released from Department of Energy functions in Oak Ridge to migrate upstream. Local soils were non-detect for this element. Mercury was detected in 17 of 61 boring samples and was not analyzed in soil.

Boron is significantly higher in ash than at other locations. This is well documented in historical samples at various TVA sites and has been reported for other sources of ash.



The levels of cadmium, chromium, copper, lead, mercury, nickel, silver, thallium and zinc in the majority of TVA ash samples were found to be within the range for soils found throughout Tennessee (TDEC 2001).

Lead, copper, nickel and chromium have similar values in the ash and in the geologic boring samples. Average values for lead and nickel are similar in all sample groups.

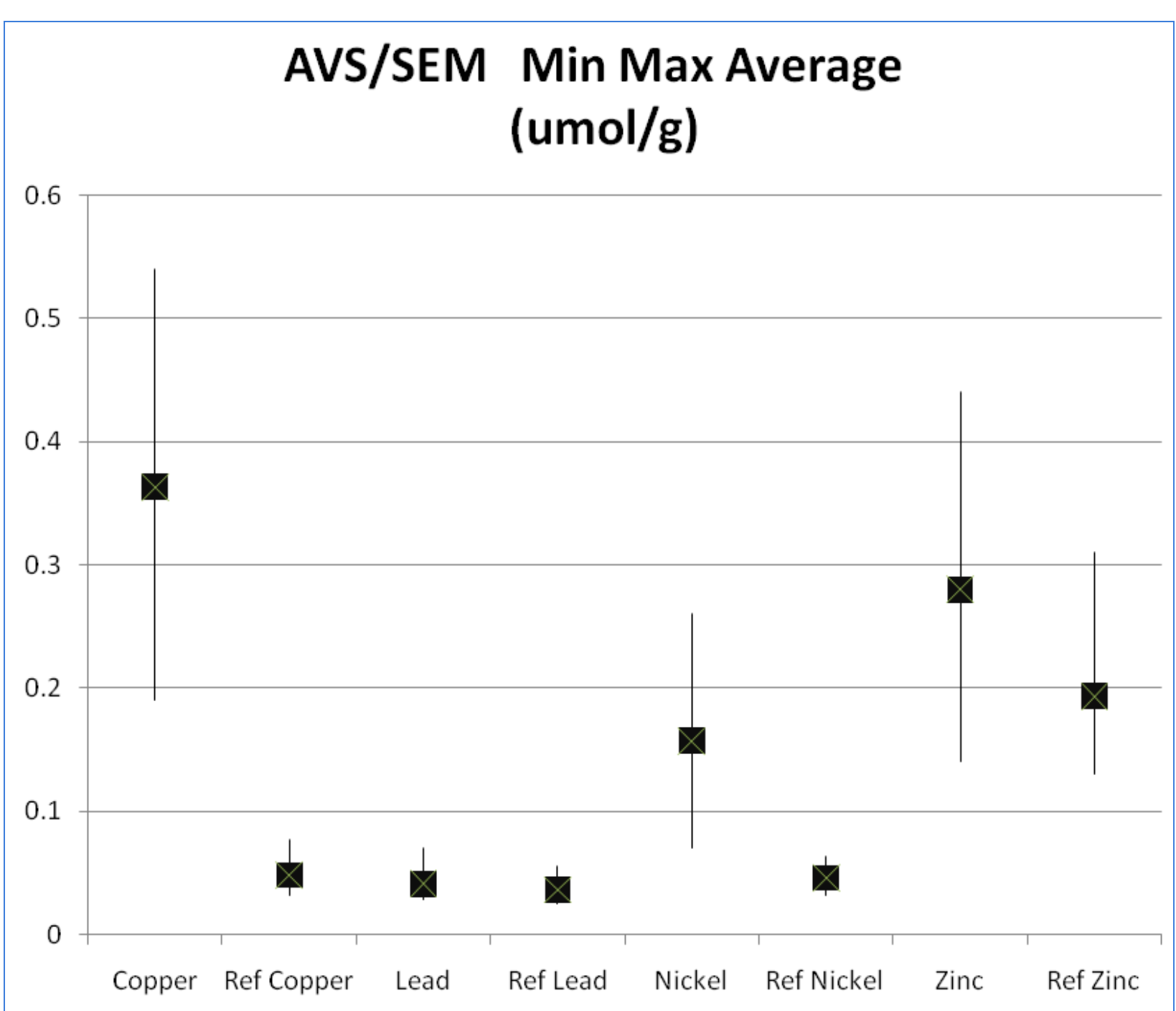


Thallium is difficult to analyze. Different detection limits on various analytical runs are notable in the graph. The only samples with detectable thallium were the ash samples with nine of 57 samples having detects. Vanadium appears slightly higher in the ash than in other sample types. Zinc values in ash appeared to match those in sediment and soil.

Footnote: The range of elemental concentrations in soil are documented in "Hazardous Trace Elements in Tennessee Soils and Other Regolith", TDEC, Division of Geology, 2001 and in "Soil Background Supplemental Data Set for the East Tennessee Technology Park, Oak Ridge, TN, Bechtel Jacobs Company LLC, 2003. See also www.tva.gov/kingston/solids.

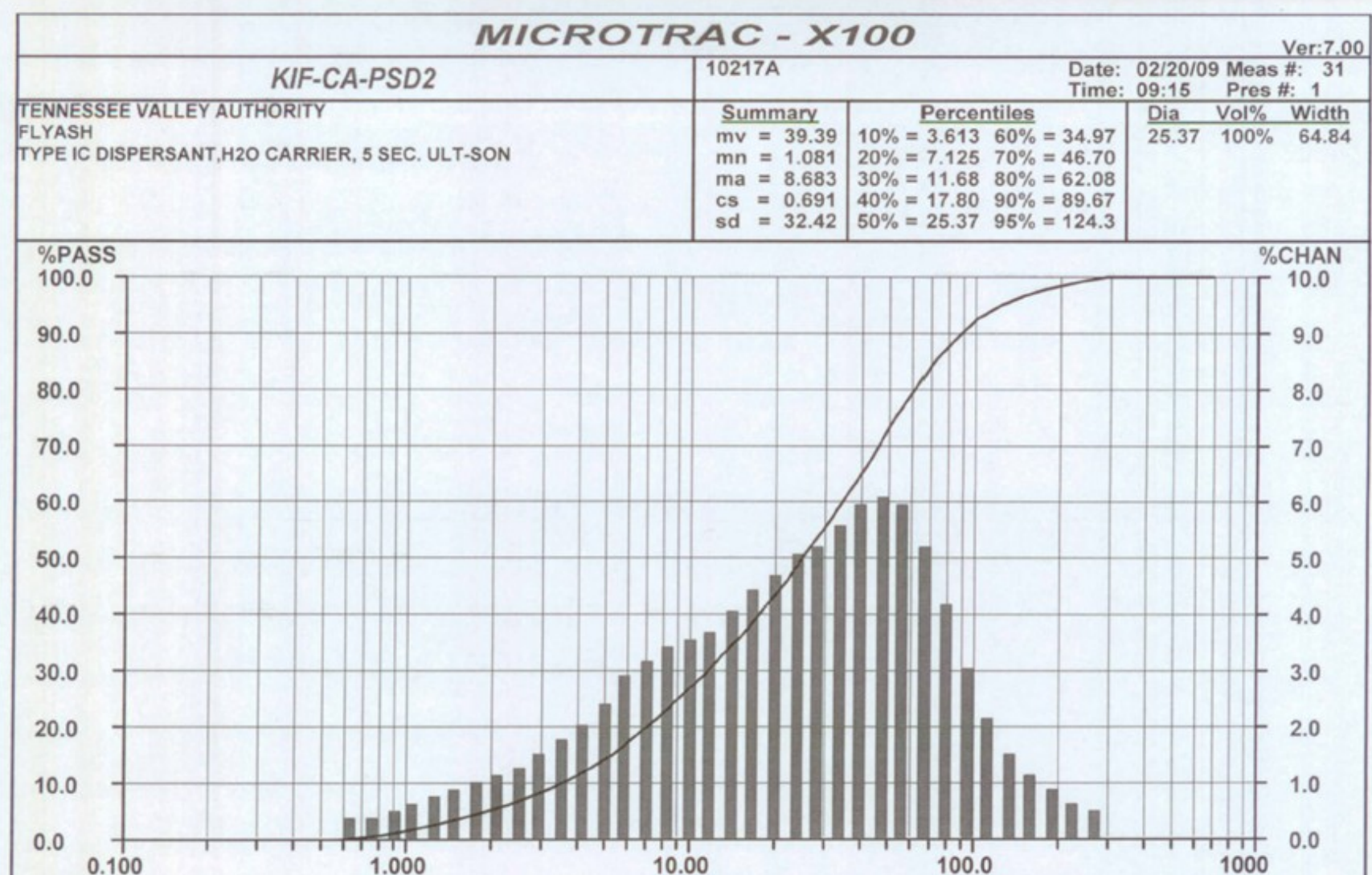
AVS/SEM

The technique called "Acid Volatile Sulfides / Simultaneously Extractable Metals (AVS/SEM)" may be used to predict the bioavailability of divalent metals to benthic organisms. When sulfide concentration is in excess of the divalent metal concentration, insoluble sulfides are expected to form, limiting the bioavailability of the metals. In the graph below, only one reference (upstream Clinch) sediment had measureable sulfide, indicating that no sulfide was present to form insoluble compounds which would limit the availability of the metals. Extractable metals indicate a difference between ash or sediments which are mostly ash and the reference sediments in the concentrations of copper and nickel. Minimum, maximum, and average values of the five metals in ash-laden deposits and reference sediments are in line with measurements of the same elements on ash and upstream sediments on the Emory River reported above.



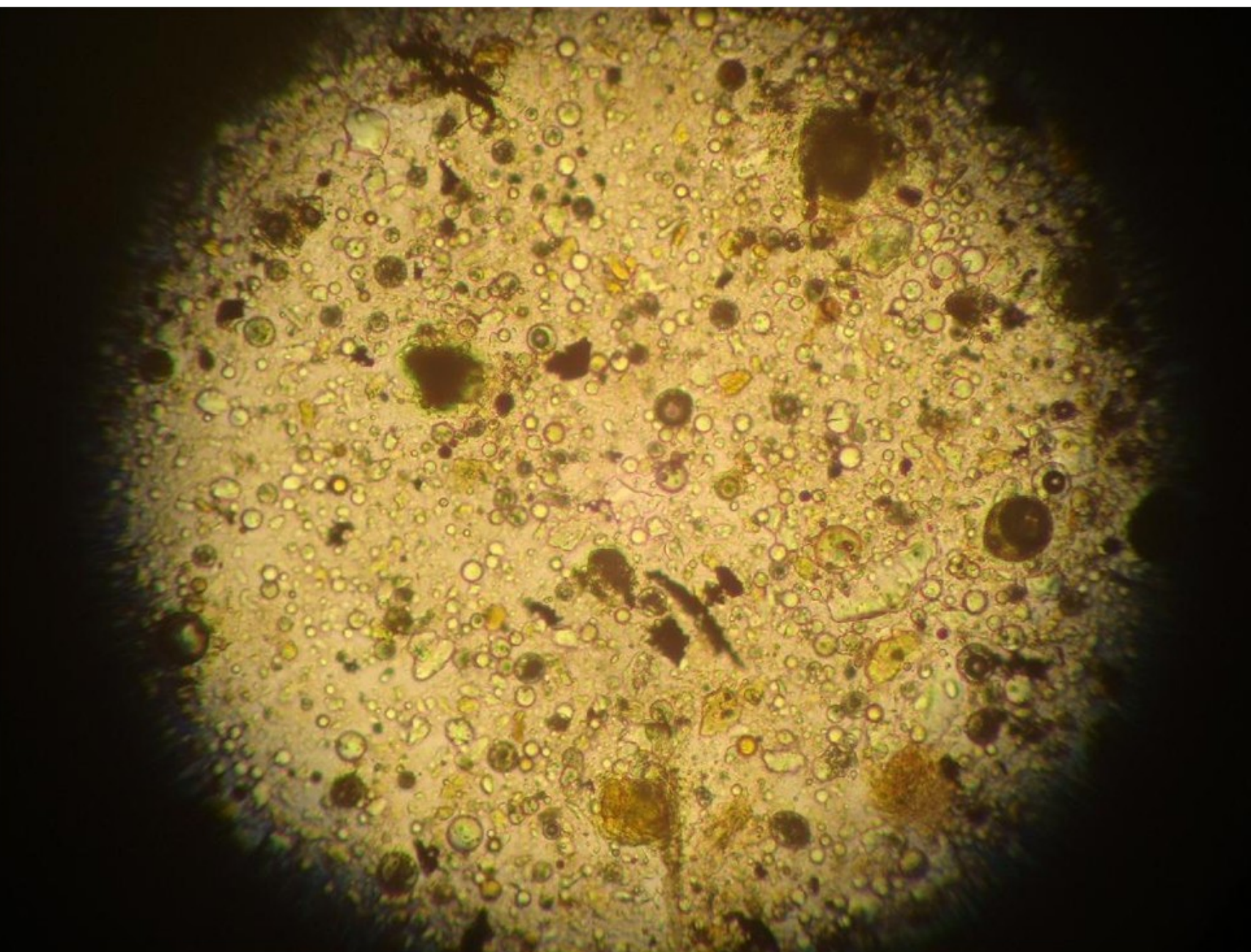
Particle Size Analysis

Particle size analysis has been carried out on the original ash material and on dredged material recovered from the Emory River. Size distributions were found to be quite variable in the undisturbed cell. Surface portions of the submerged released ash in the river were expected to be somewhat depleted in smaller particles which would have been swept downstream in early high river flow events. Transport and mixing of upstream sediments into the main body of released ash caused an increase in the sand fraction as observed in material recovered in early 2010. A graphical example of particle size study by a light scattering technique is included below for a composite sample taken from the intact cell in early 2009. The presence of smaller particle sizes was the major concern for dust control activities on the recovery site throughout 2009 and 2010.



Microscopy

Fly ash is an aluminosilicate glass consisting almost completely of spherical particles. Optical microscopy was found to be the most rapid technique to identify the presence of ash. Optical microscopy was utilized in mapping the extent and depth of ash in order to delimit dredging in the time-critical portion of the recovery activities.



Radioisotopes

Ash is known to contain naturally-occurring radionuclides, specifically isotopes of uranium, thorium, and potassium-40, and their short-lived daughter products. Initial analysis of the ash included only gamma spectroscopy which identified potassium-40, radium-226, and several of the gamma-emitting short-lived daughter products of uranium and thorium. This is consistent with results from analysis conducted by TDEC. In order to accurately characterize the activity of the uranium, thorium, and radium isotopes, which cannot be characterized using gamma spectroscopy, the additional ash samples collected by TVA were analyzed by both alpha spectroscopy and gamma spectroscopy. Results are listed in the following table. Levels of radioactivity in the ash are similar to those of typical regional soils. An exception is that levels of radium-226 generally exceed the range typical of regional soils; levels of radium-226 in regional soils are typically in the range of 0.5 to 2 picocuries per gram (pCi/g), whereas those in ash range between 4.5 and 9 pCi/g. The following table presents the range of concentrations of metals and radioisotopes found in TVA ash sampling.

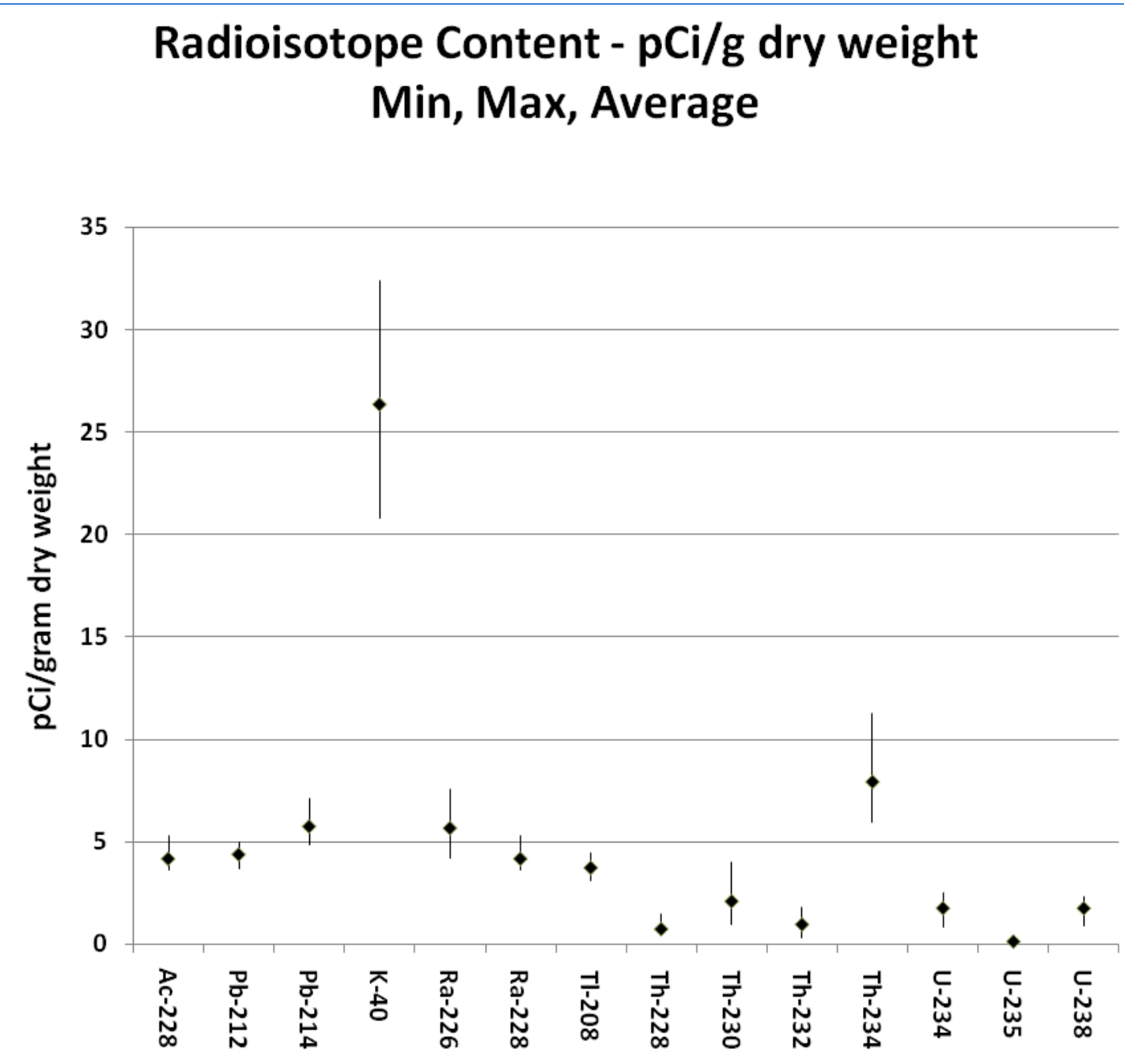


Table 1-1. Summary Statistics for Metals and Radionuclides in Ash

| Analyte | Unit | Summary Statistics for TVA Ash Data | | | | | Summary Statistics for TDEC Ash Data | | | | | Summary Statistics for EPA Ash Data | | | | |
|---------------|-------|-------------------------------------|-------------------------|-------------------------|---------------------|---------------------|--------------------------------------|-------------------------|-------------------------|---------------------|---------------------|-------------------------------------|-------------------------|-------------------------|---------------------|---------------------|
| | | Minimum Detected Result | Maximum Detected Result | Average Detected Result | Frequency of Detect | Frequency of Detect | Minimum Detected Result | Maximum Detected Result | Average Detected Result | Frequency of Detect | Frequency of Detect | Minimum Detected Result | Maximum Detected Result | Average Detected Result | Frequency of Detect | Frequency of Detect |
| Aluminum | mg/kg | ND | ND | ND | 0/52 | 0/52 | ND | ND | ND | 0/52 | 0/52 | ND | ND | ND | 0/52 | 0/52 |
| Antimony | mg/kg | ND | ND | ND | 0/52 | 0/52 | ND | ND | ND | 0/52 | 0/52 | ND | ND | ND | 0/52 | 0/52 |
| Barium | mg/kg | 69.7 | 1,410 | 710 | 52/52 | 180 | 1,100 | 358 | 12/12 | 188 | 864 | 355 | 7/7 | 7/7 | 7/7 | 7/7 |
| Boron | mg/kg | 14.5 | 212 | 99 | 45/52 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| Bromine | mg/kg | ND | ND | ND | 0/52 | 0/52 | ND | ND | ND | 0/52 | 0/52 | ND | ND | ND | 0/52 | 0/52 |
| Calcium | mg/kg | 1,450 | 30,900 | 12,081 | 52/52 | 2,000 | 27,000 | 5,325 | 12/12 | 2,190 | 19,500 | 6,156 | 7/7 | 7/7 | 7/7 | 7/7 |
| Chromium | mg/kg | 8.94 | 96 | 42 | 52/52 | 16 | 43 | 25 | 12/12 | 16.2 | 41.9 | 26.2 | 7/7 | 7/7 | 7/7 | 7/7 |
| Cobalt | mg/kg | 13.1 | 20.7 | 20.8 | 42/52 | 6.7 | 29 | 13 | 12/12 | 7.91 | 18.7 | 12.1 | 7/7 | 7/7 | 7/7 | 7/7 |
| Copper | mg/kg | 8.84 | 39 | 20 | 52/52 | 9 | 38 | 20 | 12/12 | 16.2 | 41.9 | 26.2 | 7/7 | 7/7 | 7/7 | 7/7 |
| Iron | mg/kg | 8,840 | 39,700 | 19,814 | 52/52 | 10,000 | 15,000 | 12,417 | 12/12 | 9,590 | 19,500 | 13,099 | 7/7 | 7/7 | 7/7 | 7/7 |
| Lithium | mg/kg | ND | ND | ND | 0/52 | 0/52 | ND | ND | ND | 0/52 | 0/52 | ND | ND | ND | 0/52 | 0/52 |
| Magnesium | mg/kg | 662 | 6,930 | 2,875 | 52/52 | 730 | 6,400 | 1,616 | 12/12 | 713 | 4,300 | 1,946 | 7/7 | 7/7 | 7/7 | 7/7 |
| Manganese | mg/kg | 45.5 | 698 | 139 | 52/52 | 56 | 200 | 59 | 12/12 | 45.7 | 447 | 138 | 7/7 | 7/7 | 7/7 | 7/7 |
| Mercury | mg/kg | 0.136 | 0.209 | 0.17 | 41/52 | NA | NA | NA | 0/11 | 0.0963 | 0.118 | 0.067 | 7/7 | 7/7 | 7/7 | 7/7 |
| Molybdenum | mg/kg | ND | ND | ND | 0/52 | 0/52 | ND | ND | 0/52 | 0/52 | 0/52 | ND | ND | ND | 0/52 | 0/52 |
| Nickel | mg/kg | 7.37 | 84.4 | 38.6 | 52/52 | 13 | 37 | 23 | 12/12 | 17.1 | 32.3 | 24.1 | 7/7 | 7/7 | 7/7 | 7/7 |
| Potassium | mg/kg | 642 | 7,940 | 3,551 | 52/52 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| Selenium | mg/kg | 2.64 | 17.8 | 6.7 | 45/52 | 2.2 | 2.2 | 2.2 | 11/12 | 3.13 | 7.15 | 6.88 | 7/7 | 7/7 | 7/7 | 7/7 |
| Silver | mg/kg | ND | ND | ND | 0/52 | ND | ND | ND | 0/12 | NA | NA | NA | NA | NA | NA | NA |
| Sodium | mg/kg | 283 | 7,750 | 843 | 45/52 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| Strontium | mg/kg | ND | ND | ND | 0/52 | ND | ND | ND | 0/12 | NA | NA | NA | NA | NA | NA | NA |
| Thallium | mg/kg | 2.65 | 3.8 | 3.1 | 4/52 | 1.8 | 1.8 | 1.8 | 11/12 | 4.36 | 4.36 | 4.36 | 1/7 | 7/7 | 7/7 | 7/7 |
| Uranium | mg/kg | NA | NA | NA | NA | 2.3 | 4 | 3.1 | 16/10 | NA | NA | NA | NA | NA | NA | NA |
| Vanadium | mg/kg | 15.6 | 163 | 104 | 52/52 | 42 | 150 | 77 | 12/12 | 44.6 | 121 | 73 | 7/7 | 7/7 | 7/7 | 7/7 |
| Zinc | mg/kg | 25.5 | 84.7 | 37.4 | 52/52 | 25 | 87 | 40 | 12/12 | 24.3 | 55.6 | 38.7 | 7/7 | 7/7 | 7/7 | 7/7 |
| Gross Alpha | pCi/g | NA | NA | NA | NA | 4.6 | 25 | 8.99 | 12/12 | NA | NA | NA | NA | NA | NA | NA |
| Gross Beta | pCi/g | NA | NA | NA | NA | 4.76 | 10 | 4.76 | 12/12 | NA | NA | NA | NA | NA | NA | NA |
| Acidium-228 | pCi/g | 3.63 | 5.26 | 4.24 | 11/11 | 2.47 | 3.78 | 3.08 | 12/12 | NA | NA | NA | NA | NA | NA | NA |
| Radium-226 | pCi/g | NA | NA | NA | NA | 1.71 | 2.44 | 2.08 | 12/12 | NA | NA | NA | NA | NA | NA | NA |
| Strontium-90 | pCi/g | NA | NA | NA | NA | 2.89 | 3.86 | 3.38 | 12/12 | NA | NA | NA | NA | NA | NA | NA |
| Strontium-228 | pCi/g | 4.51 | 6.62 | 5.56 | 11/11 | 2.89 | 5.98 | 3.89 | 12/12 | NA | NA | NA | NA | NA | NA | NA |
| Lead-210 | pCi/g | 3.7 | 4.98 | 4.36 | 11/11 | 2.89 | 3.86 | 3.38 | 12/12 | NA | NA | NA | NA | NA | NA | NA |
| Lead-214 | pCi/g | 4.85 | 7.1 | 5.83 | 11/11 | 3.37 | 6.52 | 4.43 | 12/12 | NA | NA | NA | NA | NA | NA | NA |
| Potassium-40 | pCi/g | 30.8 | 34.4 | 32.2 | 11/11 | 14.62 | 25.76 | 18.85 | 12/12 | NA | NA | NA | NA | NA | NA | NA |
| Radium-228 | pCi/g | 4.8 | 6.79 | 5.65 | 11/11 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| Radium-226 | pCi/g | 3.63 | 5.26 | 4.24 | 11/11 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| Thallium-208 | pCi/g | 3.11 | 4.43 | 3.4 | 10/11 | 0.89 | 1.01 | 0.94 | 12/12 | NA | NA | NA | NA | NA | NA | NA |
| Thallium-208 | pCi/g | 0.41 | 1.46 | 0.779 | 11/11 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| Thorium-230 | pCi/g | 0.44 | 1.39 | 0.71 | 11/11 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| Thorium-232 | pCi/g | 0.921 | 1.82 | 1.1 | 11/11 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| Thorium-234 | pCi/g | 0.37 | 1.13 | 0.59 | 10/11 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| Uranium-234 | pCi/g | 0.816 | 2.51 | 1.75 | 11/11 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| Uranium-235 | pCi/g | 0.0401 | 0.152 | 0.115 | 11/11 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| Uranium-238 | pCi/g | 0.855 | 2.33 | 1.72 | 11/11 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |

Ash samples collected from residential properties had results similar to those from the released ash in the embayment, and the ash remaining in the former Dredge Cell; the ash is a relatively well-mixed, homogenous material with no discernable difference in its constituent concentrations across the site.

TDEC Sampling

TDEC collected 12 ash samples on January 6 and 7, 2009. Two of the ash samples were collected from the Dredge Cell and the remaining samples were collected from surrounding residential properties. The samples were analyzed for total metals, TCLP metals, BTEX, radionuclides (gross alpha and gross beta), and PAHs. TDEC has reviewed the data and has posted relevant information on their website. As reported on their website, the ash does contain metals and radioactive materials. Table 1-1 presents the range of concentrations of metals detected in ash samples collected by TDEC. After review of the metal analyses, the only metal identified by TDEC at concentrations that may present a potential health hazard is arsenic. The TDEC ash samples contained arsenic ranging from 26 to 100 mg/kg (with an average of 73 mg/kg), which agrees with the range found in TVA sampling. TDEC did not detect any volatile organic compounds (which include BTEX) or PAHs in the ash samples.

EPA Sampling

On December 27, 2008, EPA's contractor collected two 10-point composite samples from the ash pile onsite and three grab samples of ash that had been deposited along the roadway. Samples collected on December 27, 2008, were analyzed for target analyte list metals, BTEX, silica, and TCLP metals. Table 1-1 presents the range of concentrations of metals detected in ash samples collected by EPA. Similar to TVA and TDEC sampling results, EPA testing showed arsenic to be present in the ash at levels ranging from 44.8 to 81.3 mg/kg (with an average of 61.1 mg/kg). EPA testing of the ash found no gasoline products and showed that the ash would not qualify as hazardous waste based on TCLP analysis.

Conclusion

The initial assumption following the ash release was that mixing of the various layers of ash during the release would have resulted in a relatively homogeneous material in the river. Some constituents do occur in a fairly narrow range of concentrations, and results for those might seem to support this assumption. However, closer analysis shows that while results do not span very broad ranges, there is a reasonable amount of heterogeneity in the ash deposited in the river due to less mixing of the initially deposited ash than was assumed and to particle size sorting that occurs as storm flows re-suspend and transport ash further downstream. Nevertheless, no elemental concentration or radionuclide was found to be outside the range of expected values.